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(21) International Application Number: PCT/NL99/00501 (22) International Filing Date: 6 August 1999 (06.08.99) (30) Priority Data: 1009815 6 August 1998 (06.08.98) NL		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
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(54) Title: METHOD FOR THE PRODUCTION OF AN MCFC ELECTROCHEMICAL CELL			
(57) Abstract			
<p>Method for the production of an electrochemical cell consisting of an anode and cathode separated by an electrolyte-containing matrix. With this method electrolyte is melted into the green cathode at elevated temperature to improve the stability thereof and thereafter the cell is combined and then heated. With this method the cathode can consist of two or more layers or can have been produced, starting from a mixture, by casting a tape which consists of a mixture of lithium cobaltite and carbonate. Melting-in of the electrolyte material takes place by heating in a furnace.</p>			

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Method for the production of an MCFC electrochemical cell

The present invention relates to a method according to the precharacterising clause of

Claim 1.

5. A method of this type is disclosed in EP 0 509 424 A-2. A cathode consisting of two layers is described in PCT application PCT/NL 95/00306 in the name of the Applicant (European Application no. 95930058.3). A cathode of this type is produced by placing said two layers on top of one another in the green state, for example by tape casting, and then combining the green cathode together with the other green components of the cell and heating. With this arrangements a matrix plate is present between the anode and cathode and 10 the electrolyte material is introduced into the matrix plate in the cell in some way or other during start-up.

Although an electrochemical cell of this type has an excellent performance, it has been found that problems arise during the start-up phase. In particular, during initial heating the 15 strength of the cathode is inadequate to provide for continuous contact pressure against the matrix plate. This is caused, inter alia, by the reduction in thickness of the cathode during this start-up. This reduction in thickness can be, for example, 25 %.

The production of a green tape consisting of a mixture of cathode and electrolyte constituents is described in European Application 0 509 424. The green tape is combined 20 with at least one other green tape, which comprises the anode, and heated. Melting of carbonate into the electrode will take place in the first part of the heating curve and at higher temperatures sintering takes place.

It has been found that this type of method of combination also offers inadequate guarantees for strength in respect of the tape in which the cathode is incorporated to provide 25 for continuous contact with the matrix plate.

The aim of the present invention is to prevent the disadvantages described above.

This aim is achieved with a method as described above by means of the characterising features in Claim 1.

In contrast to EP 0 509 424, in the case of the invention the electrolyte is introduced 30 into the green, i.e. unsintered, cathode material in a separate step. Such introduction can take place at elevated temperature, but this temperature is lower than the temperature at which sintering takes place. A value of 500°C for melting-in and a value of 950-1050°C for sintering may be mentioned by way of example. A sintered structure containing pores is not

produced during the first-mentioned treatment. Combination with other (green) components of the cell takes place only thereafter, preferably only after cooling of the cathode provided with electrolyte to room temperature.

The method described above imparts adequate strength to the cathode to enable the latter to be placed against the matrix with adequate contact force during start-up. The reduction in thickness that is detected during start-up is appreciably restricted, as will be illustrated in more detail below with the aid of the examples.

The green cathode described above can be any cathode known in the prior art.

According to a first variant, the cathode comprises a tape in which the carbonate (electrolyte) material has been incorporated. This tape is preferably produced by using a mixture of lithium cobaltite and carbonate particles as the starting material. This is in contrast to what is described in PCT application 94/18713, in which the starting material is cobalt particles which oxidise in the cell. Structural modifications, which have consequences for the pore size distribution, are found to take place as a result of this oxidation. This is avoided by using lithium cobaltite powder as the starting material.

According to a further advantageous embodiment, the cathode consists of a structure of at least two layers. These layers are placed on top of one another in the green state, after which melting-in of electrolyte takes place. These layers can be a layer based on lithium cobaltite and a layer containing (semi-)noble metal particles. An example thereof is a layer containing nickel particles and the last-mentioned layer will be directed towards the separator plate or current collector during use and is primarily of importance because of the conductance, whilst the layer based on lithium cobaltite is designed more in order to allow the cathodic reaction to proceed in an optimum manner.

In the latter case the method is carried out under oxidising conditions. If a tape in which the nickel layer is already present is used as the starting material, the method is carried out under a reducing atmosphere and during this procedure the electrolyte can optionally be applied as a tape.

Another possibility is that an electrolyte tape is applied to the cathode. The electrolyte tape consists of electrolyte and the electrolyte and binder are melted into the green cathode under elevated temperature. This process can take place under reducing conditions. In this case also the product thus obtained is not sintered. Sintering takes place later, either in a separate step or after combining the assembly in the electrochemical cell with anode and other components. In this context it is possible to allow the (semi-)noble metal-containing

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tape already to form part of the cathode before the electrolyte is introduced or to apply said (semi-)noble metal-containing tape only after the electrolyte has been introduced into the layer based on lithium cobaltite.

The invention will be explained in more detail below with the aid of two examples.

5

Example 1

A green lithium cobaltite tape is produced by mixing together LiCoO₂ powder, ethanol and Tween (surface-active agent). Methylcellulose (with binder), demineralised water and TBP (solvent) are then added with continuous stirring. A tape is then cast in the manner described in PCT application PCT/NL95/00306. The tape is then dried.

10 An electrolyte tape consisting of a mixture of Li₂CoO₃, Na₂CO₃ and K₂CO₃ is then placed by the tape casting technique on top of said green LiCoO₂ tape. The whole is heated in an oxidising gas atmosphere to 500 °C just above the melting point of the electrolyte and remains at this temperature for approximately 30 minutes. During this operation the liquid electrolyte transfers from the electrolyte tape into the green LiCoO₂ tape. Cooling to room temperature then takes place. It has been found that the solidified electrolyte now present in the cathode tape increases the strength of the latter and protects the lithium cobaltite during start-up in an MCFC fuel cell. Before or during the operation to incorporate the lithium cobaltite cathode, containing melted-in electrolyte, thus obtained in an MCFC, a green nickel layer with a thickness of approximately 50 µm is applied to that side which subsequently comes into contact with the current collector. Good electrical contact between current collector and cathode is ensured by this means. A 3 cm² specimen was then subjected to a start-up operation, this start-up taking place under both dry and wet nitrogen gas. In Fig. 1 the reduction in thickness of a cathode in the start-up phase is plotted as a function of the temperature, both for cathodes produced according to the prior art in combination with a separate supply of electrolyte and for cathodes according to the invention.

25 In this figure cathodes according to the prior art are indicated by a and b and a indicates start-up under dry conditions in nitrogen and b start-up under wet conditions. These results were obtained with the cell structure according to PCT application PCT/NL 95/00306. The total reduction in thickness was at least 22 % of the initial thickness.

30 Two cathodes according to the invention are indicated by c and d, c indicating dry nitrogen and d wet nitrogen. Here again start-up took place under a nitrogen atmosphere and it can be seen that a reduction in thickness of at most 5 % takes place during start-up.

Consequently, it is possible to guarantee continuous contact between cathode and other parts of the electrochemical cell during the warm-up phase. No cracking was found, whilst if the fuel gas and oxygen are then supplied and the cell is taken into operation, the performance does not differ from the performance of a fuel cell as described in PCT application PCT/NL 5 95/00306. The various aspects are illustrated with the aid of Fig. 2, where a simulation of the fuel cell with a surface area of 3 cm² obtained in this way was carried out. For this purpose use was made of so-called "simulated system conditions". The values recorded do not differ substantially from those recorded for the cell in the PCT application described above.

It has been found that despite the better yield the cathodes produced in this way have to 10 be supported during transport because of the brittleness thereof. Example 2 below was carried out in order to prevent this problem.

Example 2

The starting material used in this example is a green double tape, that is to say a tape 15 consisting of two layers, in this case a layer of lithium cobaltite and a layer of nickel particles. The LiCoO₂ tape is obtained in the manner described above.

A nickel suspension is then cast on top of this using the tape casting technique. The nickel suspension is obtained by mixing nickel powder, methylcellulose, Tween, TBP and ethanol. After some time demineralised water is added and the mixture is stirred for half an 20 hour.

After a green double tape has been obtained in this way, an electrolyte tape consisting of a mixture of Li₂CoO₃, Na₂CO₃ and K₂CO₃ is applied thereto. The electrolyte tape is placed 25 on the lithium cobaltite part of the double tape. Melting-in of the electrolyte then takes place, that is to say electrolyte moves from the electrolyte tape to the LiCoO₂ layer as a result of heating under a reducing gas atmosphere to just above the melting point of the electrolyte 500 °C. Heating takes place for 30 minutes. Ultimately the electrolyte penetrates not only into the LiCoO₂ layer but also into the nickel layer.

Cooling to room temperature then takes place. The electrolyte solidified in the cathode 30 imparts strength to the cathode and protects the LiCoO₂ against reduction during start-up in the fuel cell. Because the green LiCoO₂/Ni tape is placed with the nickel side against a current collector when applying the electrolyte tape, said current collector can give the package that is thus obtained strength during subsequent transport and contact between the nickel layer and the current collector is optimised.

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It has been found that an MCFC cell obtained with the aid of this method has the same good characteristics as the MCFC cell described on the basis of Example 1.

From these two examples and the other part of the description it will be clear to those skilled in the art that numerous variations are possible without going beyond the scope of the invention as described in the appended claims.

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Claims

1. Method for the production of an MCFC electrochemical cell, comprising the provision of an anode and green cathode combined as an assembly and separated by a matrix plate with electrolyte, based on carbonate, as well as a separator plate, the electrolyte being introduced into the green cathode and the part thus obtained being combined with the anode and heated, characterised in that the introduction of electrolyte into the cathode comprises melting-in at elevated temperature.
5
2. Method according to Claim 1, wherein, after melting-in at elevated temperature, the part thus obtained is cooled to room temperature before combining with the other components of the cell.
10
3. Method according to one of the preceding claims, wherein a tape comprising a mixture of lithium cobaltite and carbonate is provided.
4. Method according to one of the preceding claims, wherein said cathode comprises at least two layers, a layer based on LiCoO₂ and a layer containing (semi-)noble metal particles, wherein said layer containing (semi-)noble metal particles is directed towards said separator plate and the electrolyte is melted into said LiCoO₂ layer.
15
5. Method according to Claim 4, wherein the electrolyte is melted into the green layer based on LiCoO₂, after which the green layer containing (semi-)noble metal particles is applied thereon.
20
6. Method according to Claim 5, wherein the introduction of electrolyte is carried out under oxidising conditions.
7. Method according to Claim 4, wherein a green cathode consisting of at least two layers is provided, into which the electrolyte is introduced and wherein the layer containing (semi-)noble metal is placed against the separator plate/current collector, after which the assembly is combined.
25
8. Method according to Claim 7, wherein the introduction of electrolyte takes place under a reducing atmosphere.
9. Method according to one of the preceding claims, wherein the electrolyte comprises a mixture of carbonates containing at least Li₂CoO₃.
30
10. Method according to one of the preceding claims, wherein said (semi-)noble metal-containing particles comprise nickel.

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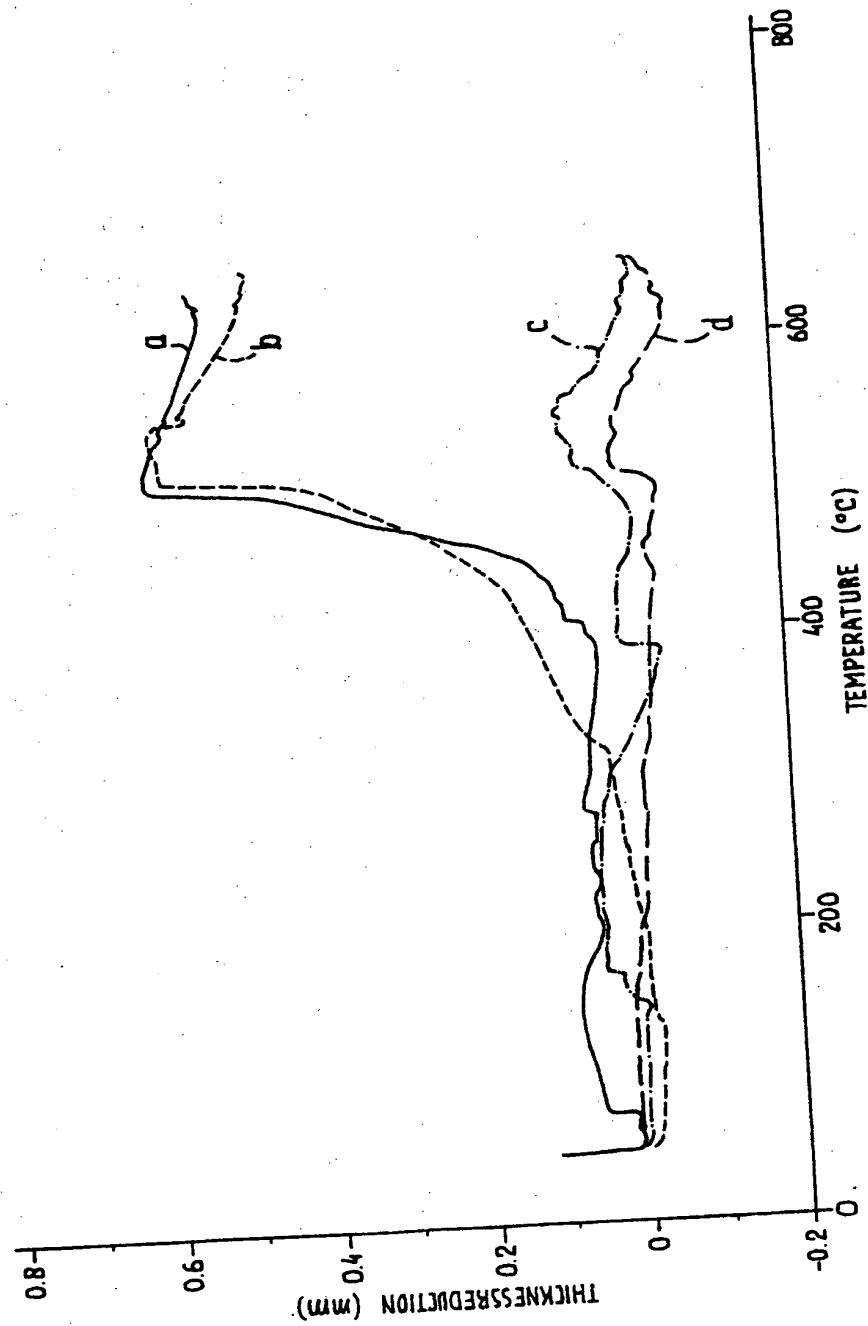


Fig-1

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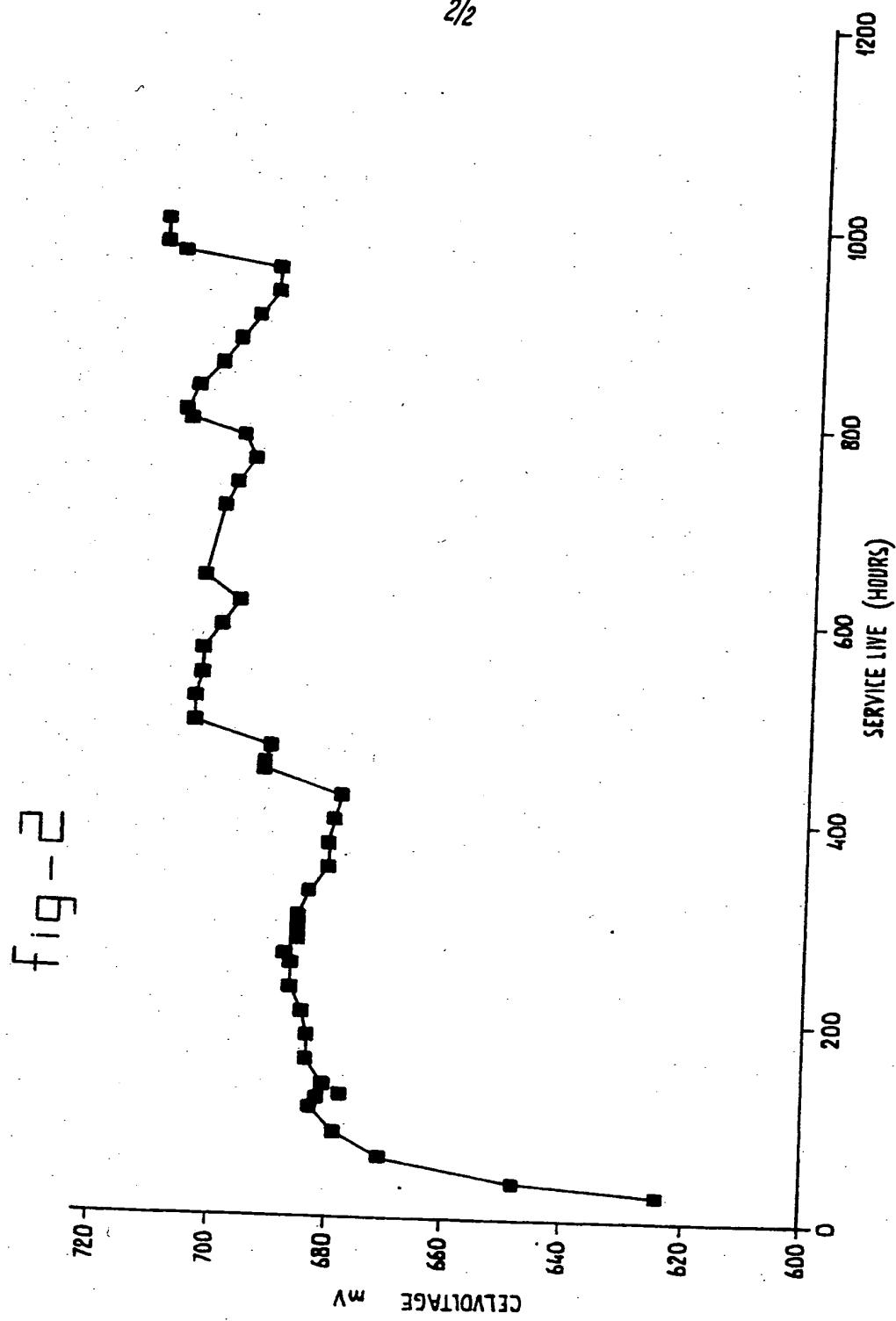


Fig - 2

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INTERNATIONAL SEARCH REPORT

Int. Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M8/14 H01M4/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 509 424 A (INST GAS TECHNOLOGY) 21 October 1992 (1992-10-21) cited in the application column 4, line 27 - line 37 column 8, line 8 - line 26; example VI -/-</p>	1,9

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Int. Search Application No
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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 109, no. 2, 11 July 1988 (1988-07-11) Columbus, Ohio, US; abstract no. 9417, NIIKURA JUNJI ET AL: "Electrodes for molten-carbonate fuel cells" XP002125957 abstract -& PATENT ABSTRACTS OF JAPAN vol. 12, no. 291 (E-644), 9 August 1988 (1988-08-09) & JP 63 066858 A (MATSHUSITA ELECTRIC IND CO), 25 March 1988 (1988-03-25) abstract</p> <p>—</p> <p>NIIKURA J ET AL: "FABRICATION AND PROPERTIES OF COMBINED ELECTRODE/ELECTROLYTE TAPE FOR MOLTEN CARBONATE FUEL CELLS" JOURNAL OF APPLIED ELECTROCHEMISTRY, vol. 20, no. 4, 1 July 1990 (1990-07-01), pages 606-610, XP000453540 page 606, right-hand column, paragraph 1 - paragraph 3 page 607, right-hand column, paragraph 3 page 608, left-hand column, paragraph 1</p> <p>—</p> <p>WO 96 08050 A (STICHTING ENERGIE ;SITTERS ERIC FRANCISCUS (NL); HEUVELN FREDERIK) 14 March 1996 (1996-03-14) cited in the application column 4, line 5 - line 25; claims 1,5</p> <p>—</p> <p>US 4 891 280 A (KAUN THOMAS D ET AL) 2 January 1990 (1990-01-02) column 3, line 47 - line 63; claim 1</p> <p>—</p> <p>PATENT ABSTRACTS OF JAPAN vol. 098, no. 008, 30 June 1998 (1998-06-30) & JP 10 074529 A (TOSHIBA CORP), 17 March 1998 (1998-03-17) abstract</p> <p>—</p> <p>PATENT ABSTRACTS OF JAPAN vol. 017, no. 214 (E-1357), 27 April 1993 (1993-04-27) & JP 04 351854 A (MITSUBISHI ELECTRIC CORP), 7 December 1992 (1992-12-07) abstract</p> <p>—</p> <p>US 5 468 573 A (BREGOLI LAWRENCE J ET AL) 21 November 1995 (1995-11-21) column 1, line 46 - line 58; claim 1</p>	1,9
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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